



# Interfacial coupling effects in g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> nanocomposites with enhanced H<sub>2</sub> evolution under visible light irradiation

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## ABSTRACT

The g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> nanocomposite is an important material in photocatalysis, but little attention has been paid to their interfacial interaction in photocatalytic reaction. Herein, we prepare the g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> nanocomposites via a two-step mechanically milling and calcination process. The composite exhibited the highest H<sub>2</sub> evolution activity superior to that of the pure g-C<sub>3</sub>N<sub>4</sub> and SrTiO<sub>3</sub> in the visible light. The results of UV–vis DRS, PL and photoelectrochemical measurements demonstrated that g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> exhibited more visible light adsorption and faster photo-generated charge transfer. Furthermore, the interfacial electronic structures of g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> nanocomposites were thoroughly characterized. According to the XPS and DFT results, with the help of a strong built-in electric field presenting in the g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> interface, the photo-generated electrons flow to the SrTiO<sub>3</sub> from g-C<sub>3</sub>N<sub>4</sub>, leading to the highly-efficient electron separation and more H<sub>2</sub>O molecules photo-reduction to H<sub>2</sub>. This work explicates the significant role of built-in electric field in H<sub>2</sub> evolution on g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> photocatalyst.

## 1. Introduction

With the limitations of the fossil fuel and the increasing CO<sub>2</sub> emissions, finding the clean, renewable and carbon-neutral alternative energy sources is urgently needed to satisfy growing energy demand. The photocatalytic H<sub>2</sub> evolution from water splitting with the use of solar energy is considered as a promising way, because of no destructive by-products generation and environmental friendliness. Therefore, photocatalysis technology is believed as a potential method in the face of our energy and environmental challenges in the near future. Wide bandgap semiconductors such as TiO<sub>2</sub>, ZnO, etc. [1–5] have been explored a great deal, but their main issue is that the photocatalytic response is mainly initiated in the near-UV or UV region. Therefore, developing visible-light-driven photocatalysts is an efficient approach.

Recently, many visible-light-driven semiconductor photocatalysts have been investigated [6,7]. Among them, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has attracted a lot of attention due to its good photoactivity, chemical stability, narrow band gap, and low cost [8–10]. The g-C<sub>3</sub>N<sub>4</sub> is composed of 2D sheets with tri-s-triazine subunits connected through planar tertiary amino groups in a layer. Importantly, g-C<sub>3</sub>N<sub>4</sub> possesses a

band gap of ca. 2.7 eV, which enables it to be a visible-light-active photocatalyst for photochemical reactions and solar energy conversion [11], such as water splitting [12,13], organic pollutant mineralization [14], and CO<sub>2</sub> conversion. [15] Nevertheless, single g-C<sub>3</sub>N<sub>4</sub> is still far from ready to be used in real application due to its high recombination rate of photo-generated electron-hole pairs [16]. Many efforts have been employed to enhance the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>, such as metal/nonmetal doping [17,18], nanostructuring [19], and coupling it with other materials [20]. As one of the effective strategies to enhance the separation and transportation of photo-generated electron-hole pairs, coupling with another semiconductor has been reported. Zhao et al. successfully prepared CdMoO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> composites [21], which exhibited 4.8 times of CO<sub>2</sub> conversion rate higher than those of g-C<sub>3</sub>N<sub>4</sub>. He et al. synthesized ZnO/g-C<sub>3</sub>N<sub>4</sub> photocatalyst [22], yielding 4.9 times higher than the pure g-C<sub>3</sub>N<sub>4</sub> in photocatalytic CO<sub>2</sub> reduction. Shi et al. reported hollow-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composites [23], in which N-TiO<sub>2</sub> acts as an electron trapping site, leading to higher photocatalytic H<sub>2</sub> evolution. The above results indicate that coupling of semiconductors might be a suitable option to improve the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>.

The SrTiO<sub>3</sub> photocatalyst has attracted considerable attention, due

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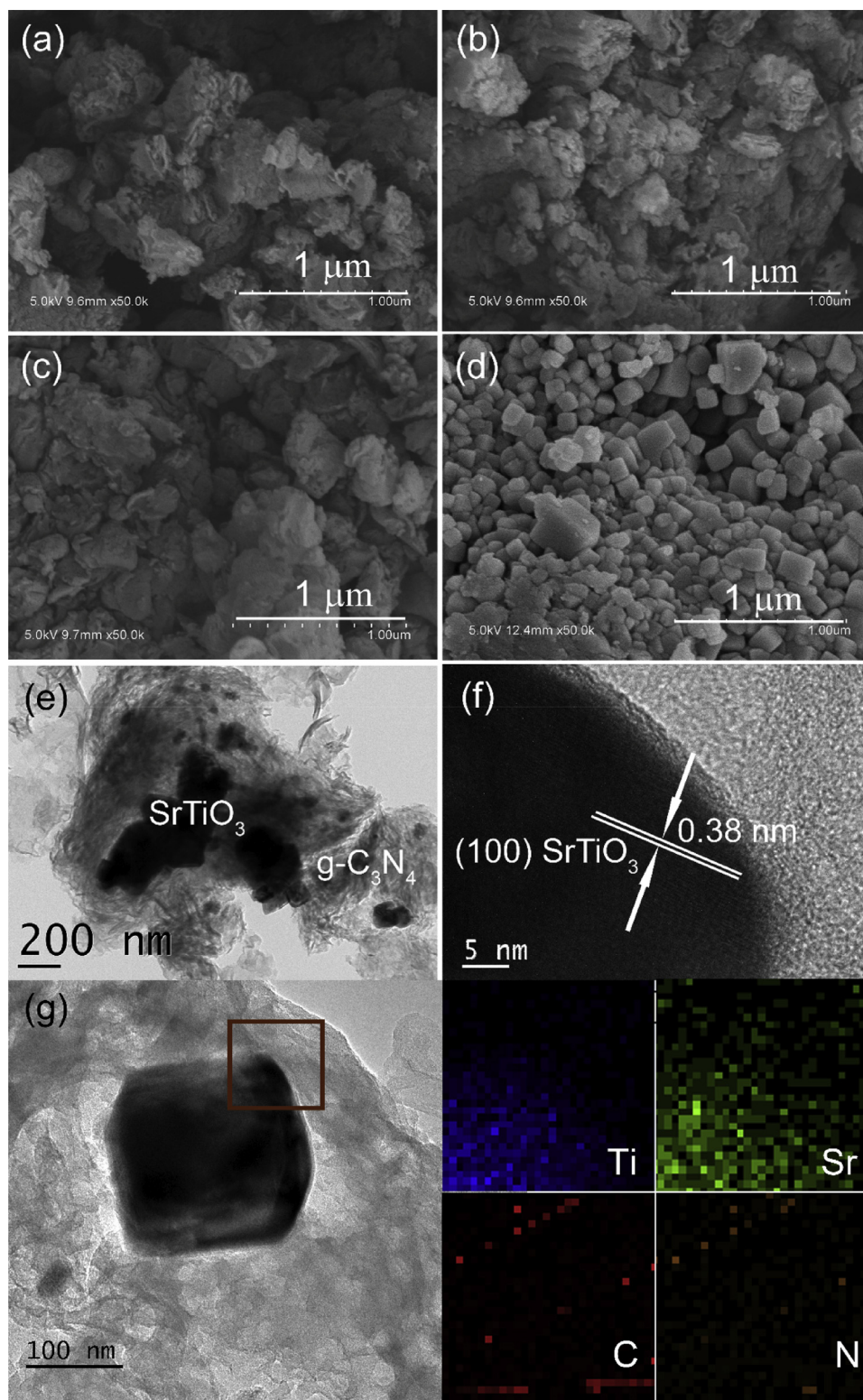
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**Fig. 1.** SEM images of the prepared samples: (a) 3% SrTiO<sub>3</sub>-CN, (b) 5% SrTiO<sub>3</sub>-CN, (c) 10% SrTiO<sub>3</sub>-CN, and (d) SrTiO<sub>3</sub>. TEM image of (e) 5% SrTiO<sub>3</sub>-CN and HRTEM image of (f) 5% SrTiO<sub>3</sub>-CN. (g) HAADF-STEM-EDS elemental mapping of 5% SrTiO<sub>3</sub>-CN.

to its excellent optical, chemical, and electronic structural properties [24,25]. As a prominent photocatalysts for reduction reactions, Rh-doped SrTiO<sub>3</sub> afforded significantly high efficiency for H<sub>2</sub> evolution under visible light [26]. The Rh and Au on SrTiO<sub>3</sub> photocatalyst achieved significant enhancement and high selectivity for syngas yield from the reduction of CO<sub>2</sub> and H<sub>2</sub>O mixture under visible-light

irradiation [27]. N-doped SrTiO<sub>3</sub> nanoparticles wrapped in g-C<sub>3</sub>N<sub>4</sub> nanosheets hybrid nanocomposites exhibited an improved photocatalytic activity for pollutants degradation [28]. In addition, g-C<sub>3</sub>N<sub>4</sub> coated SrTiO<sub>3</sub> was synthesized by decomposing urea in the presence of SrTiO<sub>3</sub>, and it possessed a higher H<sub>2</sub> production rate [29]. However, the interfacial electronic effects of the g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> are still worthy to be

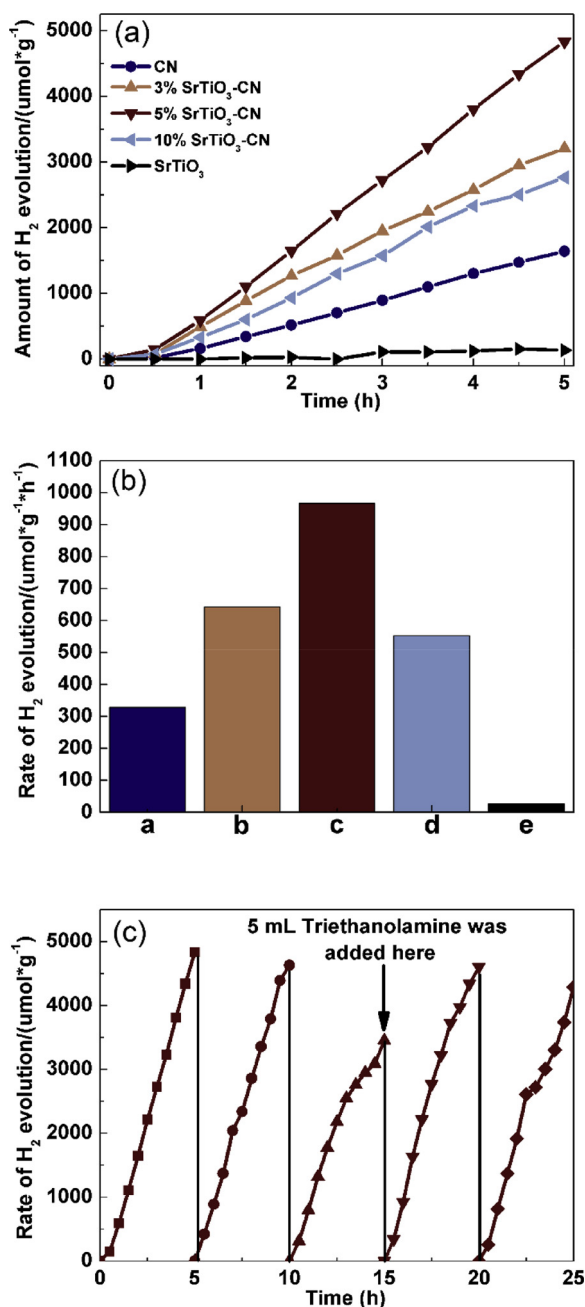


Fig. 2. (a) Time courses of photocatalytic H<sub>2</sub> evolution, (b) average rate of H<sub>2</sub> evolution over different photocatalysts, and (c) repeated time courses of photocatalytic H<sub>2</sub> evolution on 5% SrTiO<sub>3</sub>-CN. The samples labeled: (a) CN, (b) 3% SrTiO<sub>3</sub>-CN, (c) 5% SrTiO<sub>3</sub>-CN, (d) 10% SrTiO<sub>3</sub>-CN, (e) SrTiO<sub>3</sub>.

investigated.

In this paper, we focused on the synergistic interaction between SrTiO<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> interface, and the relationships between structures, properties and photocatalytic performances were explored. The g-C<sub>3</sub>N<sub>4</sub> sheets were coupled with SrTiO<sub>3</sub> via ball milling and subsequently calcination, and the phase structure, chemical composition, morphology and photocatalytic H<sub>2</sub> evolution activity of the nanocomposite were investigated in detail. Furthermore, the possible mechanisms of the enhancement of photocatalytic activity have also been provided. This work highlights the effect of interfacial coupling between g-C<sub>3</sub>N<sub>4</sub> and SrTiO<sub>3</sub>, and it would provide a new insight into the construction of stable and high efficient visible-light photocatalysts.

## 2. Experimental section

### 2.1. Synthesis of SrTiO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites

All the chemicals were of analytical grade and used without further purification. Deionized water was used in all the experiments.

The g-C<sub>3</sub>N<sub>4</sub> was synthesized by calcinating urea (Aladdin) as a precursor [30]. Typically, 10 g urea was heated to 520 °C with a heating rate of 5 °C min<sup>-1</sup> and maintained at 520 °C for 2 h in a muffle furnace. The calcination process was in a covered crucible to prevent sublimation, and then the yellow powder was obtained.

In the typical synthesis of SrTiO<sub>3</sub>, SrCO<sub>3</sub> (1 mmol, Aladdin), Rutile (1 mmol, Aladdin), NaCl (50 mmol, Aladdin), and KCl (50 mmol, Aladdin) were mixed and carefully ground. And the mixture was heated at 900 °C with a heating rate of 5 °C min<sup>-1</sup> and maintained at 900 °C for 5 h under static air. After cooling down to room temperature, the sample was washed with deionized water several times to remove residual salt impurity and dried in an oven at 60 °C for 24 h.

The preparation of SrTiO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites was done as follows: in brief, an appropriate amount of SrTiO<sub>3</sub> powder and g-C<sub>3</sub>N<sub>4</sub> (0.5 g) were mixed and mechanically milled in high energy mill machine for 30 min, and then calcined at 520 °C for 2 h under static air. The hybrid nanocomposites with 3 wt%, 5 wt% and 10 wt% of SrTiO<sub>3</sub> are referred to as 3% SrTiO<sub>3</sub>-CN, 5% SrTiO<sub>3</sub>-CN, and 10% SrTiO<sub>3</sub>-CN, respectively. As a reference, g-C<sub>3</sub>N<sub>4</sub> was milled without SrTiO<sub>3</sub> and calcined for comparison, and the obtained product was named as CN.

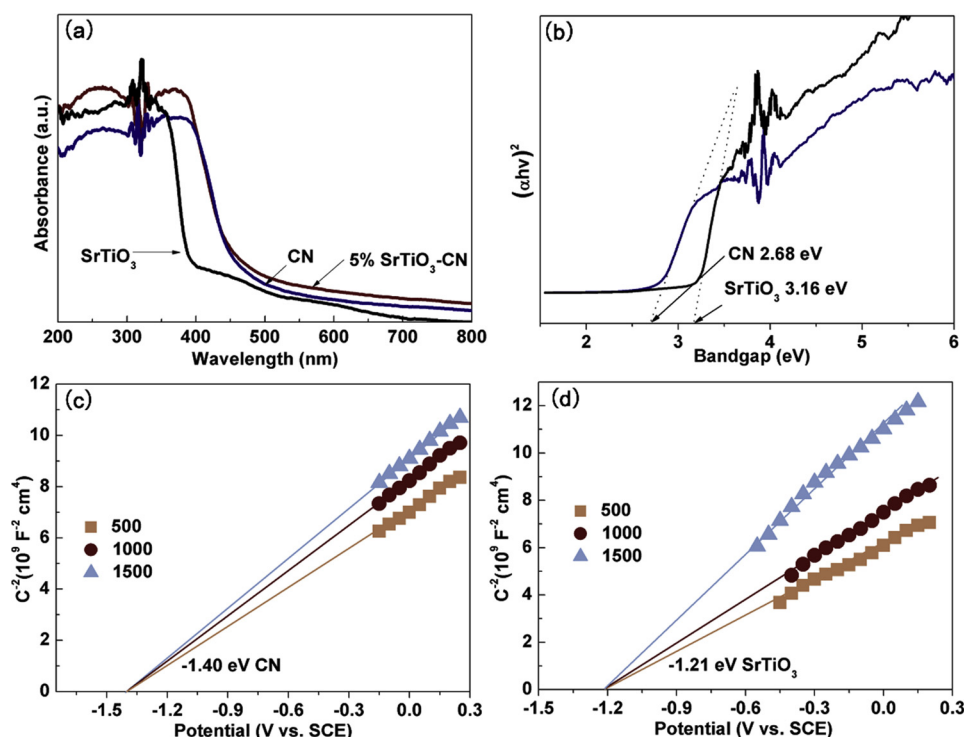
### 2.2. Characterizations

The crystal structures were recorded by X-ray diffraction (XRD) with Philips X'Pert Pro diffractometer by Ni-filtered Cu Kα radiation (λ = 0.15418 nm). Scanning electron microscopy (SEM) experiment was obtained on a Hitachi S-4800 electron microscope operated at beam energy of 10.0 kV. The catalysts were gold-coated for about 100 Å thick in a BAL-TEC SCD-500 device. Transmission electron microscopy (TEM) image was obtained on JEM-2100 instrument at an accelerating voltage of 200 kV. The samples were crushed and dispersed in A.R. grade ethanol and the resulting suspensions were dried on carbon film supported copper grids. HAADF-STEM-EDS elemental mapping analysis was performed on a double-aberration corrected Titan<sup>TM</sup> cubed G2 60–300 S/TEM equipped with Super-X<sup>TM</sup> technology. X-ray photoelectron spectroscopy (XPS) analysis was performed on PHI 5000 VersaProbe high performance electron spectrometer with an Al Kα radiation (1486.6 eV) achromatic X-ray source. The samples were out-gassed at room temperature in a UHV chamber. The charging effect of samples was compensated with C 1s peak at 284.6 eV based on the adventitious carbon. Brunauer–Emmet–Teller (BET) surface area was examined by nitrogen adsorption at 77 K on Micrometrics ASAP-2020 adsorption apparatus. Before each adsorption measurement, approximate 0.15 g catalyst was degassed in the N<sub>2</sub>/He mixture at 90 °C for 4 h. Surface areas were estimated by using the BET method. The FT-IR spectra were measured from 400 to 4000 cm<sup>-1</sup> at the spectral resolution of 4 cm<sup>-1</sup> on Nicolet 5700 FT-IR spectrometer. The samples (5 mg) were mixed with KBr and pressed into self-supported pellets. UV–vis diffuse reflectance spectroscopy (UV–vis DRS) were recorded in the range of 200–800 nm by a Shimadzu UV-2401 spectrophotometer with the reference of BaSO<sub>4</sub>. Photoluminescence (PL) spectra were determined on the Fluoromax-4 fluorescence spectrophotometer. The wavelength of the excitation light was 325 nm. The experiments were carried out in the solid state. The slit in all measurements was 1.5 nm. The PL spectra was measured from 350 nm to 750 nm.

### 2.3. Photoelectrochemical measurements

Electrochemical measurements were carried out on a CHI660 A electrochemical workstation (Shanghai Chenhua Instrument, Inc.





**Fig. 3.** (a) UV–vis absorption spectra of the CN, 5% SrTiO<sub>3</sub>-CN, and SrTiO<sub>3</sub> photocatalysts. (b) Band gap energies of CN and SrTiO<sub>3</sub>. Mott-Schottky plots of (c) CN and (d) SrTiO<sub>3</sub> at frequency 0.5 kHz, 1.0 kHz, and 1.5 kHz.

China) using a standard three-electrode cell. The prepared samples were deposited on In-doped SnO<sub>2</sub>-coated glass (ITO glass) electrode as the working electrodes with an active area of ca. 1 cm<sup>2</sup>, with a Pt wire as the counter electrode, saturated calomel electrode (SCE) as a reference electrode, and 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution as electrolyte. A 300 W Xe lamp with the 420 nm cut-off filter served as a light source. The working electrodes were prepared as follows: 2 mg photocatalyst was grounded with 5 mL ethanol and 10  $\mu$ L 5% Nafion (DuPont) to make a slurry. Afterwards, the slurry was coated onto a 1 cm<sup>2</sup> × 1.5 cm ITO glass electrode. After air-drying, the working electrode was further dried at 393 K for 2 h to improve adhesion. Finally, a homogeneous film can be obtained. The transient photocurrent densities of the as-prepared electrodes were tested at 0.5 V versus saturated calomel electrode under visible light irradiation. The Mott-Schottky curves were taken under dark with a voltage of 5 mV at a frequency of 1.5, 1.0, and 0.5 kHz. The potential ranged from −1.5 to 1.0 V (vs. SCE).

#### 2.4. Photocatalytic H<sub>2</sub> generation testing

The photocatalytic hydrogen evolution reactions were carried out in a top-irradiation type vessel linked to a gas-closed glass system Ceaulight CEL-SPH2N-D (Ceaulight, Beijing, China) under an irradiation of 300 W Xe lamp with the 420 nm cut-off filter. The light intensity was 467 mW. 50 mg catalyst was dispersed in 100 mL aqueous solution containing triethanolamine (10 vol%) as a sacrificial electron donor. The H<sub>2</sub>PtCl<sub>6</sub> (398  $\mu$ L, 10 g/L) aqueous solution was added and then was in-situ reduced to Pt (3 wt% Pt) cocatalyst during the reaction. The temperature of the solution was kept at 6 °C. The reaction system was sealed and evacuated for 30 min before illumination. The amount of generated hydrogen was determined online by a gas chromatograph equipped with a thermal conductive detector (TCD). Argon was used as the carrier gas of the gas chromatography.

#### 2.5. Calculation method and model

The Vienna Ab Initio Simulation Package (VASP) [31,32] for all the

spin-polarized DFT calculations within the generalized gradient approximation (GGA) using the PBE functional formulation were used in this work [33]. Projected augmented wave (PAW) pseudopotentials was employed to describe the interactions between ionic cores and valence electrons. 4 (C), 5 (N), 6 (O), 4 (Ti) and 10 (Sr) valence electrons were explicitly taken into account [34]. The valence electronic states were expanded in plane wave basis sets with a cutoff energy of 450 eV. The DFT-D3(BJ) method was used to describe the dispersion effects in the system [35]. Partial occupancies of electronic bands were allowed with the Gaussian smearing method and a width of 0.01 eV. A  $p(1 \times \sqrt{2})$  supercell with a single-layered corrugated g-C<sub>3</sub>N<sub>4</sub> sheet and A  $p(2 \times 3)$  supercell with six atomic-layered SrTiO<sub>3</sub>(001) were used, and the vacuum between slabs was 25 Å, in which a Monkhorst-Pack K-point mesh of  $4 \times 3 \times 1$  was included.

### 3. Results and discussion

#### 3.1. Crystal structure, morphology and texture properties

The crystal structure, morphology and texture properties of the as-prepared SrTiO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposites were determined by a series of characterization methods. The XRD patterns of CN, SrTiO<sub>3</sub>-CN, and SrTiO<sub>3</sub> samples are shown in Fig. S1. The XRD patterns of CN showed two peaks at  $2\theta = 13.1^\circ$  and  $27.5^\circ$ , which are corresponded to the (100) and (002) planes of g-C<sub>3</sub>N<sub>4</sub>, respectively. The (100) plane with the average interlayer distance ( $d = 0.675$  nm) belongs to the in-plane repeating units of the heptazine heteroatom cycles, and the (002) plane with  $d = 0.324$  nm is related to the graphitic layer stacking, similar to graphite [11,36]. The cubic taunonite SrTiO<sub>3</sub> (JCPDS No. 35-0734) was identified in the pristine SrTiO<sub>3</sub> and SrTiO<sub>3</sub>-CN samples, and the peak intensity of SrTiO<sub>3</sub> gradually increased with the SrTiO<sub>3</sub> content. It was found that the position of SrTiO<sub>3</sub> characteristic diffraction peaks in SrTiO<sub>3</sub>-CN samples remained the same as those in pristine SrTiO<sub>3</sub>, which indicated that the introduction of g-C<sub>3</sub>N<sub>4</sub> did not destroy the crystal structure of SrTiO<sub>3</sub> in all SrTiO<sub>3</sub>-CN samples.

FT-IR spectra of CN, SrTiO<sub>3</sub>, and SrTiO<sub>3</sub>-CN composites were

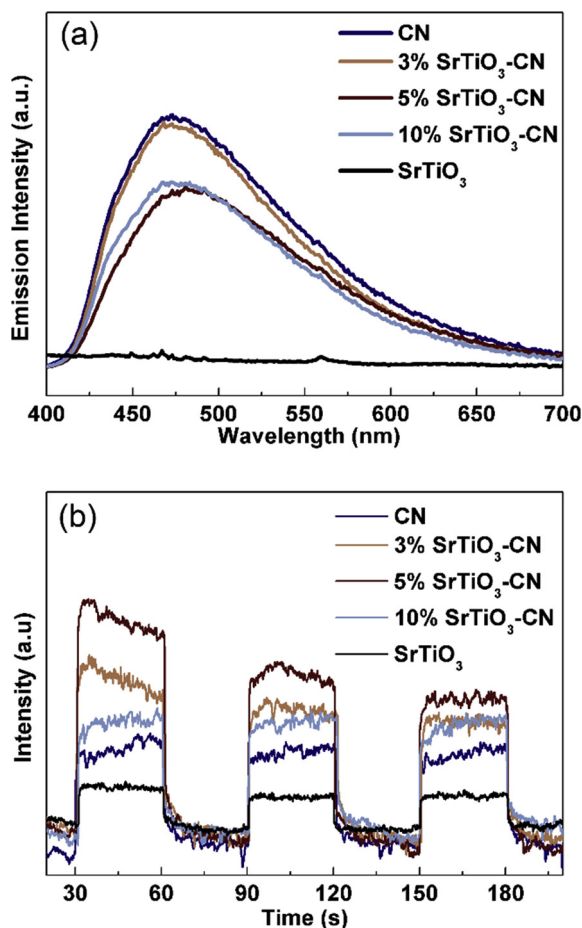


Fig. 4. (a) Room temperature PL spectra under the excitation wavelength of 325 nm and (b) Transient photocurrent response of CN, 3% SrTiO<sub>3</sub>-CN, 5% SrTiO<sub>3</sub>-CN, 10% SrTiO<sub>3</sub>-CN, and SrTiO<sub>3</sub> photocatalysts.

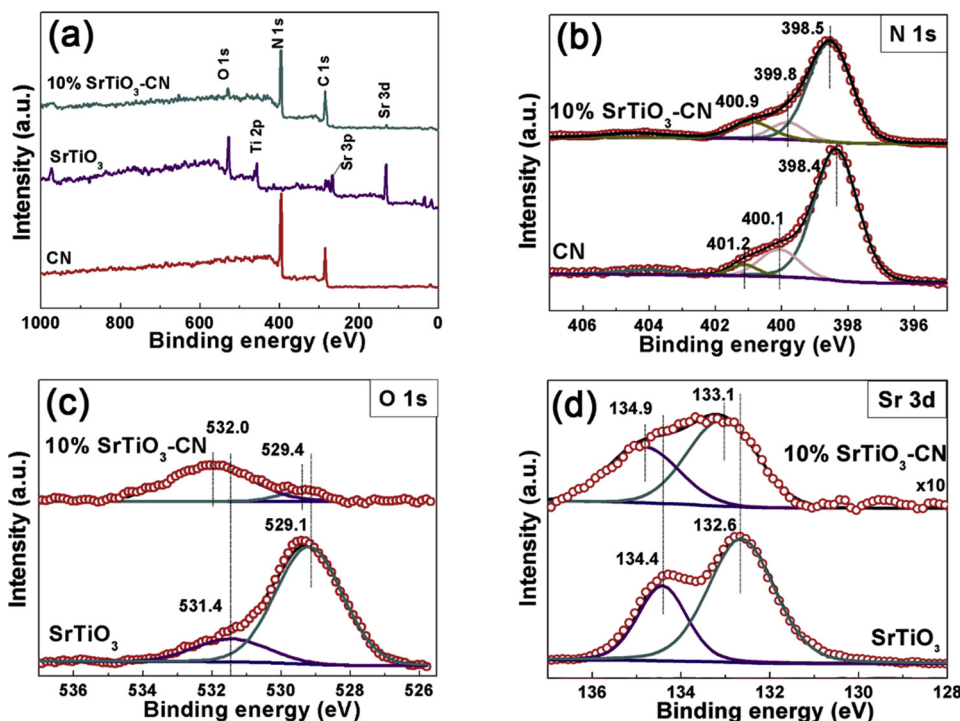
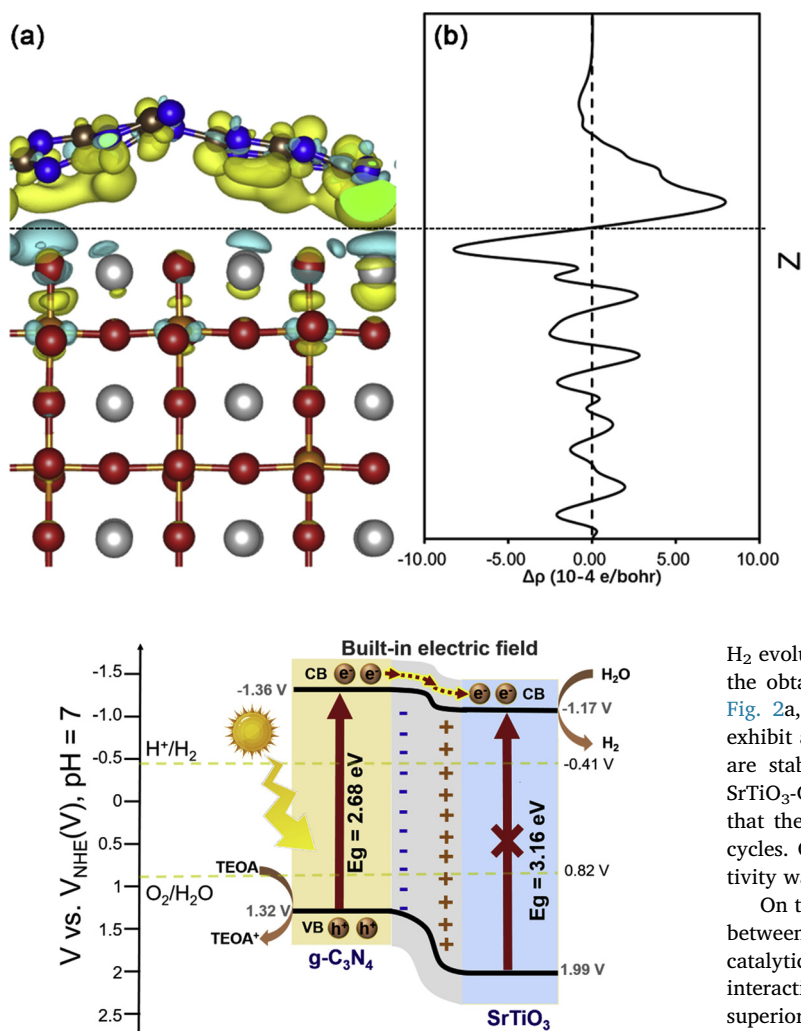


Fig. 5. (a) XPS survey spectrum of CN, 10% SrTiO<sub>3</sub>-CN, and SrTiO<sub>3</sub>. High-resolution XPS spectra of prepared samples: (b) N 1s, (c) O 1s, (d) Sr 3d.

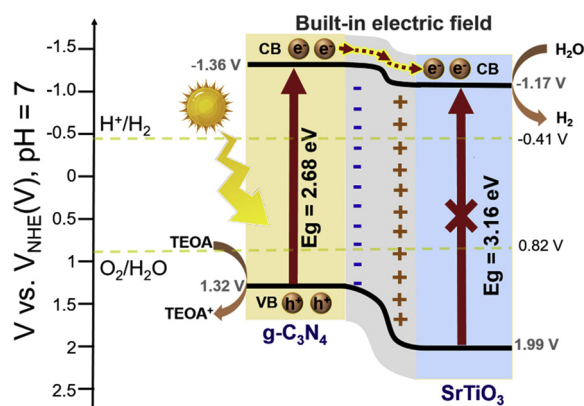
presented in Fig. S2. For CN sample, the broad peak between 3600 and 2900 cm<sup>-1</sup> is related to the stretching vibration modes of the N–H and O–H stretches of the adsorbed H<sub>2</sub>O. The prominent peaks at 1237, 1319, 1414, 1572, and 1638 cm<sup>-1</sup> correspond to typical stretching vibration modes of C=N and C–N heterocycles. [37] The peak at 809 cm<sup>-1</sup> is assigned to the out-of-plane bending vibration of the s-triazine ring. For the pristine SrTiO<sub>3</sub> sample, the peak at about 600 cm<sup>-1</sup> is assigned as the characteristic peak TiO<sub>6</sub> of SrTiO<sub>3</sub> [38]. Furthermore, when the SrTiO<sub>3</sub> are coupled with g-C<sub>3</sub>N<sub>4</sub>, the vibration peak attributed to SrTiO<sub>3</sub> weaken and broaden, which indicated that the interaction of SrTiO<sub>3</sub>-CN on the interface was present.

The morphology and microstructure of CN, SrTiO<sub>3</sub>-CN, and SrTiO<sub>3</sub> photocatalysts were characterized by SEM. As shown in Fig. S3, the accumulated layered structure of CN was observed, owing to the planar graphitic-like structure. The pristine SrTiO<sub>3</sub> sample shows cubic morphology (Fig. 1d). After combining with g-C<sub>3</sub>N<sub>4</sub> (Fig. 1a–c), the SrTiO<sub>3</sub> nanoparticles are covered by g-C<sub>3</sub>N<sub>4</sub>. Fig. 1e and f show the transmission electron microscopy (TEM) images of 5% SrTiO<sub>3</sub>-CN. A lattice spacing of 0.38 nm in Fig. 1f corresponding to the (001) crystal facet of SrTiO<sub>3</sub> (No. 35-0734) is clearly observed in 5% SrTiO<sub>3</sub>-CN, in accordance with the XRD result. Since the (001) facet of SrTiO<sub>3</sub> has the lowest energy, it is expected that SrTiO<sub>3</sub> nanocube was primarily exposed with (001) facets [39]. In Fig. 1e, it is observed that the soft g-C<sub>3</sub>N<sub>4</sub> nanosheets completely coat the SrTiO<sub>3</sub> particles. The HAADF-STEM-EDS elemental mapping images of Sr, Ti, C, and N in Fig. 1g further confirm the good coating of g-C<sub>3</sub>N<sub>4</sub> on the surface of SrTiO<sub>3</sub> in SrTiO<sub>3</sub>-CN heterostructure. The tight coupling is favorable for the charge transfer between g-C<sub>3</sub>N<sub>4</sub> and SrTiO<sub>3</sub>. Thus, we can conclude that the interface structure was mainly constructed by the SrTiO<sub>3</sub> (001) facets and g-C<sub>3</sub>N<sub>4</sub>.

In order to characterize the specific surface area and pores properties of the as-prepared CN, SrTiO<sub>3</sub>-CN, and SrTiO<sub>3</sub> photocatalysts, we carried out the N<sub>2</sub> adsorption analysis. The nitrogen adsorption-desorption isotherms (Fig. S4a) and Barret–Joyner–Halenda (BJH) pores size distribution curves (Fig. S4b) of CN, SrTiO<sub>3</sub> and SrTiO<sub>3</sub>-CN samples reveal that the all samples exhibit type IV isotherms with distinct H3 hysteresis loops, which are characteristics of mesoporous materials



**Fig. 6.** (a) The isosurface map of charge density differences for  $g\text{-C}_3\text{N}_4/\text{SrTiO}_3$ , the isosurface value is  $0.001 \text{ e}/\text{\AA}^3$ . The cyan and yellow regions represent the electron depletion and accumulation, respectively. The C, N, O, Ti and Sr atoms are represented as brown, blue, red, yellow and silver, respectively. (b) Planar averaged charge density difference as a function of fractional position in the Z-direction (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



**Fig. 7.** Proposed mechanism for enhanced photocatalytic  $\text{H}_2$  evolution in  $\text{SrTiO}_3\text{-CN}$  composites.

[40,41]. CN and  $\text{SrTiO}_3\text{-CN}$  samples show almost the same adsorption-desorption isotherms and pore size distribution curves. In addition, the Brunauer-Emmett-Teller (BET) specific surface areas of CN, 3%  $\text{SrTiO}_3\text{-CN}$ , 5%  $\text{SrTiO}_3\text{-CN}$ , 10%  $\text{SrTiO}_3\text{-CN}$ , and  $\text{SrTiO}_3$  samples are calculated to be 31.9, 32.4, 30.9, 29.4, and  $6.4 \text{ m}^2/\text{g}$ , respectively. As we all know, the high surface area can provide more active sites and make the composites photocatalytic process more efficient. Thus, the results of pore size and specific surface area reveal that surface area may not be the main reason for the enhanced photocatalytic activity of  $\text{SrTiO}_3\text{-CN}$  composites.

### 3.2. Photocatalytic $\text{H}_2$ evolution

The photocatalytic activity of the prepared samples toward water splitting was evaluated in the presence of 10 vol% triethanolamine (TEOA) as a sacrificial agent and 3 wt% platinum as a co-catalyst under visible light irradiation. The average photocatalytic  $\text{H}_2$ -evolution rates over various photocatalysts are displayed in Fig. 2b in comparison. The  $\text{SrTiO}_3$  shows the lowest  $\text{H}_2$ -generation activity for its low visible-light absorption, and other  $\text{H}_2$ -evolution rates were measured to be 641.8, 966.8, 553.4, and  $328.4 \mu\text{mol g}^{-1} \text{h}^{-1}$  for 3%, 5%, 10%  $\text{SrTiO}_3\text{-CN}$ , and CN, respectively. The results demonstrate that although the photocatalytic performance of  $\text{SrTiO}_3$  is poor and the combination of  $\text{SrTiO}_3$  is beneficial for the enhanced activity compared to the pure CN. Furthermore, the 5%  $\text{SrTiO}_3\text{-CN}$  sample exhibited the superior activity for

$\text{H}_2$  evolution than other  $\text{SrTiO}_3\text{-CN}$  samples. Moreover, the stability of the obtained catalysts in the reaction is determined. As observed in Fig. 2a, the rates of hydrogen evolution over the prepared samples exhibit a linear increase in the reactions, implying that photocatalysts are stable under light illumination. The photocatalytic test of 5%  $\text{SrTiO}_3\text{-CN}$  in 5 cycles was further carried out (Fig. 2c), it demonstrated that the hydrogen evolution activity was unchanged in the first two cycles. Once TEOA was added in the reaction, the photocatalytic activity was recovered. Thus, the 5%  $\text{SrTiO}_3\text{-CN}$  has good photostability.

On the basis of the above results, it was deduced that the interface between  $\text{SrTiO}_3$  and CN would play a key role in the enhanced photocatalytic performance, and thus the relationships between interfacial interaction and chemical properties are explored in detail. Generally, superior  $\text{H}_2$  evolution performance was mainly attributed to the large surface area, available visible light absorption, and highly-effective charge separation. From the results of surface area, it is concluded that the specific surface area may not be the reason for the enhanced photocatalytic activity of  $\text{SrTiO}_3\text{-CN}$ .

### 3.3. Optical and photoelectrochemical properties

The optical absorption properties of the as-synthesized samples were studied by UV–vis diffuse reflectance spectroscopy. As observed in Fig. 3a, CN absorbs the light from UV to visible region at 460 nm, owing to the charge transfer from the valence band (VB) to the conduction band (CB). Whereas,  $\text{SrTiO}_3$  can only absorb the light with  $\lambda < 390 \text{ nm}$ , due to its wide band gap. However, in the present of CN, more visible light is absorbed by  $\text{SrTiO}_3\text{-CN}$ . The band gap values ( $E_g$ ) of the samples are determined by the tangent lines of  $(ah\nu)^2$  against energy ( $h\nu$ ), as shown in Fig. 3b [42–44]. The estimated band-gap values are ca. 2.68 and 3.16 eV corresponding to CN and  $\text{SrTiO}_3$ , respectively.

In addition, the Mott-Schottky (M-S) plots are employed to determine the types of conductivity for CN and  $\text{SrTiO}_3$  as well as their flat-band potential ( $E_{\text{fb}}$ ). As shown in Fig. 3c and d, the results show that the positive slopes correspond to n-type property of CN and  $\text{SrTiO}_3$  [45]. Moreover, the flat potentials for CN and  $\text{SrTiO}_3$  are  $-1.40$  and  $-1.21 \text{ V}$  versus SCE, respectively. It is known that the conduction band potentials ( $E_{\text{CB}}$ ) for n type semiconductor is more negative about  $-0.1$  or  $-0.2 \text{ V}$  than its flat band potential [46]. And thus, the  $E_{\text{CB}}$  for CN and  $\text{SrTiO}_3$  are roughly reckoned up to be  $-1.60$  and  $-1.41 \text{ V}$  versus SCE, that is  $-1.36$  and  $-1.17 \text{ V}$  vs. normal hydrogen electrode (NHE) ( $E_{\text{NHE}} = E_{\text{SCE}} + 0.241 \text{ V}$ ). The valence band (VB) potentials of CN and  $\text{SrTiO}_3$



are 1.32 and 1.99 V versus NHE calculated by the equation:  $E_{VB} = E_{CB} + E_g$ . The above Type-II band alignment is beneficial for the proper electrons-holes transfer in the interface of the composites, and thus the photocatalytic activity is enhanced.

Photoluminescence (PL) spectra is a well-known method to explore both transfer process of the charge carrier on interface and the recombination rate involved with the photogenerated electron-hole pairs. Herein, the PL spectra are employed to reveal the recombination abilities of the SrTiO<sub>3</sub>-CN composites. Fig. 4a presents the PL spectra of the CN, SrTiO<sub>3</sub>-CN, and SrTiO<sub>3</sub> photocatalysts at an excitation wavelength of 325 nm. The PL intensity of SrTiO<sub>3</sub> is very low, owing to the highly crystalline, ordered cubic structure with less extrinsic defects of SrTiO<sub>3</sub> after calcination at 900 °C. The emission band for pristine CN was centered at 460 nm, which was attributed to the radiative recombination process of self-trapped excitations. Noteworthy, the PL intensity of the SrTiO<sub>3</sub>-CN heterostructures decreased compared to CN, and 5% SrTiO<sub>3</sub>-CN shows the lowest PL intensity in all composites. The fluorescence quenching via coupling SrTiO<sub>3</sub> mainly results from improved interfacial charge transfer between SrTiO<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>, which could improve the separation of photo-excited electron-hole pairs, leading to the enhanced photocatalytic activity.

In addition, the transient photocurrent responses of pristine CN, SrTiO<sub>3</sub>-CN, and SrTiO<sub>3</sub> photocatalysts electrodes were determined (Fig. 4b). As expected, the SrTiO<sub>3</sub>-CN composites exhibit the higher photocurrent response than that of pristine CN and SrTiO<sub>3</sub>, which indicates the higher separation efficiency of photogenerated carriers on the interface of the composites. With increasing the content of SrTiO<sub>3</sub>, there is a peak value for the photocurrent intensity, and the 5% SrTiO<sub>3</sub>-CN displays the highest photocurrent respond. The photocurrent values in 3% SrTiO<sub>3</sub>-CN and 5% SrTiO<sub>3</sub>-CN decrease with irradiation time, which indicates that the recombination of photogenerated electron-hole pairs occurs in the process. The photoelectrons recombine with the holes which accumulated on the surface of the samples rather than trapped by reduced species in the electrolyte, thus the photo current decays [47–49]. Based on the above results, it is suggested that the superior interfacial coupling between SrTiO<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> has a positive influence on visible light absorption and photo-generated electrons-holes transfer, and then enhances the photocatalytic H<sub>2</sub> evolution.

### 3.4. Interfacial interactions of SrTiO<sub>3</sub>-CN

In order to gain further insight into the interfacial electronic structures, we use the XPS technology to investigate the surface electronic structure and bonding configuration of SrTiO<sub>3</sub>-CN composites. The survey XPS spectra of the CN, 10% SrTiO<sub>3</sub>-CN, and SrTiO<sub>3</sub> samples are shown in Fig. 5a. For the SrTiO<sub>3</sub>-CN sample, the peaks attributed to C, N, Sr, O elements were observed in survey XPS spectra, whereas, the Ti signal was found in the high-resolution XPS spectra (Fig. S5b). In Fig. S5a, the high-resolution C 1s spectrum in CN could be divided into two main peaks centered at ca. 284.6 and 288.0 eV. The weak peak at 284.6 eV is responsible for the adventitious carbon in g-C<sub>3</sub>N<sub>4</sub>, which is determined as standard carbon [50]. The strong peak at 288.0 eV was assigned to sp<sup>2</sup>-bonded carbon atoms in the heterocycle (N–C=N) of the aromatic g-C<sub>3</sub>N<sub>4</sub>, which is the major skeleton carbon in the triazine-based heterocycle [8]. Compared to CN sample, the binding energy of the N–C=N groups on SrTiO<sub>3</sub>-CN was barely shifted. Furthermore, the N 1s XPS spectra for CN and SrTiO<sub>3</sub>-CN are displayed in Fig. 5b. The N 1s spectrum of CN is deconvoluted to three peaks at 398.4, 400.1, and 401.2 eV. The dominant peak at 398.4 eV is assigned to sp<sup>2</sup>-hybridized nitrogen (pyridine N) in triazine rings (C–N=C). [51]. The peak at 400.1 eV corresponds to ternary nitrogen (pyrrolic N) bonded to carbon atoms in the form of N–(C)<sub>3</sub> [52]. The pyridine N and pyrrolic N together with N–C=N form the heptazine heterocyclic ring units, which are the main substructure of g-C<sub>3</sub>N<sub>4</sub>. The peak at 401.2 eV is related to the presence of amino groups (graphitic N, C–N–H) [53]. After combined with SrTiO<sub>3</sub>, the peaks attributed to pyrrolic N [N–(C)<sub>3</sub>] and graphitic N

(C–N–H) were shifted to the lower binding energies, indicated that the electrons from SrTiO<sub>3</sub> flowed into the triazine rings of CN between SrTiO<sub>3</sub>-CN interface. The pyridine N was barely shifted on SrTiO<sub>3</sub>-CN, which indicated a weak interaction between pyridine N and SrTiO<sub>3</sub>. A similar phenomenon has also been reported between CoP/g-C<sub>3</sub>N<sub>4</sub> [54].

In the O 1s spectrum of SrTiO<sub>3</sub> (Fig. 5c), the asymmetric peak at 529.1 eV is assigned to the O<sup>2–</sup> species binding energy characteristic of oxide materials. [43] The shoulder peak observed at 531.4 eV can be attributed to the chemisorbed oxygen species on surface [55]. The peak of lattice oxygen O<sup>2–</sup> species (529.4) in SrTiO<sub>3</sub>-CN exhibits a positive shift relative to that of SrTiO<sub>3</sub> (around 529.1 eV), as well as a positive shift of chemisorbed oxygen, suggesting that electrons on the O atoms of SrTiO<sub>3</sub> in composites are lost. In the fitting peaks of Sr 3d (Fig. 5d) in SrTiO<sub>3</sub> sample, a major peak at 132.6 eV with a shoulder at 134.4 eV are ascribed to the 3d<sub>5/2</sub> and 3d<sub>3/2</sub> core level of Sr<sup>2+</sup> [56]. The binding energies of Sr 3d<sub>5/2</sub> and Sr 3d<sub>3/2</sub> of SrTiO<sub>3</sub>-CN are located at 133.1 and 134.9 eV, which are 0.5 eV higher than in SrTiO<sub>3</sub> sample. Combined with the XPS results of N 1s and C 1s, it was suggested that electrons on O and Sr atoms (SrTiO<sub>3</sub>) are donated to the ring of the s-triazine (g-C<sub>3</sub>N<sub>4</sub>) on the SrTiO<sub>3</sub>-CN interface.

In order to further confirm the interfacial electronic interaction of the nanocomposites, the variation of electronic density of the SrTiO<sub>3</sub>-CN nanocomposites was calculated. This can be expressed as (as shown in Fig. 6):  $\Delta\rho = \rho(g\text{-C}_3\text{N}_4/\text{SrTiO}_3) - \rho(g\text{-C}_3\text{N}_4) - \rho(\text{SrTiO}_3)$ , where  $\rho(\text{SrTiO}_3/g\text{-C}_3\text{N}_4)$  is the electron density of the total g-C<sub>3</sub>N<sub>4</sub>/SrTiO<sub>3</sub> system, and  $\rho(\text{SrTiO}_3)$  and  $\rho(g\text{-C}_3\text{N}_4)$  are the unperturbed electron densities of the SrTiO<sub>3</sub> (001) and g-C<sub>3</sub>N<sub>4</sub> sheet, respectively. In Fig. 6a, the cyan and yellow regions represent the electron depletion and accumulation, respectively. A strong regions of charge accumulation is found on the g-C<sub>3</sub>N<sub>4</sub>, whereas the charge depletion appears on the Sr and O atoms of SrTiO<sub>3</sub>. Fig. 6b plots the planar averaged charge density difference along the direction perpendicular to the SrTiO<sub>3</sub> (001) surface. The positive and negative values represent electron accumulation and depletion, respectively. The electron accumulation on g-C<sub>3</sub>N<sub>4</sub> and depletion of SrTiO<sub>3</sub> clearly demonstrated that the electrons transfer from the SrTiO<sub>3</sub> to g-C<sub>3</sub>N<sub>4</sub>. The electron distribution variation of g-C<sub>3</sub>N<sub>4</sub> after combined with SrTiO<sub>3</sub> was shown in Fig. S6. The average electron accumulation of pyrrolic N and graphitic N c-N and graphitic- was much greater than pyridine N, which confirmed the XPS results. Based the above results, the photo-generated electron will transfer from g-C<sub>3</sub>N<sub>4</sub> to SrTiO<sub>3</sub> in composites, which is due to the built-in electric field caused by these electronic interactions at the interface [57]. The built-in electric field at the interface as a driving force for the transfer of the photo-generated electrons improved the charge separation and photocatalytic activity of H<sub>2</sub> evolution.

Meanwhile, the type II heterojunction between g-C<sub>3</sub>N<sub>4</sub> and SrTiO<sub>3</sub> was illustrated in Fig. 7 [58]. According to the results of band gap energy and flat-band potential, the band structures of CN and SrTiO<sub>3</sub> were described. The reduction level for H<sub>2</sub> is positioned below the CB of CN and SrTiO<sub>3</sub>, and the oxidation level for H<sub>2</sub>O to O<sub>2</sub> is above the VB of CN and SrTiO<sub>3</sub>. These band positions permit the transfer of electrons and holes for water splitting. It could be observed that upon visible light photoexcitation, electrons and holes are first generated in the CB and VB of g-C<sub>3</sub>N<sub>4</sub> not SrTiO<sub>3</sub> of SrTiO<sub>3</sub>-CN composites. The electrons excited from the surface of g-C<sub>3</sub>N<sub>4</sub> can transfer to the CB of SrTiO<sub>3</sub> via the heterojunction interface, because of the lower CB position of SrTiO<sub>3</sub> and the driving force of the interfacial built-in electric field. Subsequently, the electrons flowed into the CB of SrTiO<sub>3</sub> can be transferred to the surface, in order to the reduction of adsorbed water molecules to hydrogen. On the other hand, photogenerated holes in the VB of CN are trapped by scavenger triethanolamine. Hence, the built-in electric field in the interface of SrTiO<sub>3</sub>-CN composites decreases the recombination rate of photogenerated electrons and enhances visible-light harvesting, which results in superior photocatalytic activity for the SrTiO<sub>3</sub>-CN heterojunction.

## 4. Conclusions

In summary, SrTiO<sub>3</sub>-CN nanocomposite photocatalysts with the contents of SrTiO<sub>3</sub> in the 1–10 wt% range were synthesized via mechanically milling and subsequently calcination process. Among all the prepared samples, 5% SrTiO<sub>3</sub>-CN exhibits the best photocatalytic performance than that of CN and SrTiO<sub>3</sub>, because of the formation of a type II heterojunction and the built-in electric field in interface. And the intensive interfacial electronic effects are beneficial for the faster photo-generated electron transfer and carrier separation, and enhanced photocatalytic H<sub>2</sub> evolution.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.01.089>.

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